

AN INVESTIGATION OF THE CHEMISTRY OF CATALYTIC PRELIQUEFACTION

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INTRODUCTION

Direct coal liquefaction processes which have been developed over the years have been based on the philosophy of high temperature homolytic cleavage of bonds to yield free radicals which are capped by hydrogen from the donor solvent or hydroaromatic structures in coals. While low rank coals offer the potential of high oil yields because of their small aromatic ring cluster size, it has been observed that under conditions optimized for bituminous coals, low rank coals appear harder to liquefy (1,2). For example, Derbyshire and Whitehurst (3) demonstrated that low rank coals produce very low conversions in short contact time liquefaction in a donor solvent or in long time liquefaction in a non-donor solvent. For low rank coals and lignites, it appears likely that crosslinking reactions associated with oxygen functional groups (4,5) occur before the homolytic cleavage reactions, and if not controlled, can limit the maximum conversion of coal to liquids.

It has been observed that in single stage coal liquefaction, bond breaking, crosslinking and hydrogen transfer reactions are carried out simultaneously. This does not enable each individual reaction to be optimized. Recent research on "temperature staged liquefaction" routes, exploring the effects of catalyst and solvent has been pursued using tubing bomb experiments at Penn State University by Derbyshire, Davis, Schobert and co-workers (6-12). The tubing bomb results (6) showed that liquefaction of a low rank coal at 350°C in naphthalene with a Mo catalyst resulted in improved yields with higher fractions of oils in subsequent liquefaction at 425°C.

The objective of this work was the identification and optimization of the beneficial preliquefaction chemistry through the application of advanced analytical techniques and theoretical models which have been previously employed to understand and predict coal pyrolysis and fluidity behavior. The analytical techniques include three methods to determine the functional group composition of the preliquefaction products: 1) Quantitative Fourier Transform Infrared (FT-IR) spectroscopy (13-16); 2) Cross-polarization-magic angle spinning (CP/MAS) NMR with dipolar dephasing (17-21); and 3) Thermogravimetric analysis with detection of the evolved products by FT-IR spectroscopy (TG-FTIR) (22,23); 4) Field Ionization Mass Spectroscopy (FIMS), a method to determine the molecular weight distribution of soluble products (24-27); and 5) Solvent swelling to determine the degree of crosslinking in the preliquefaction residue (28,29).

The theoretical model describes the break up of the coal macromolecular network under the influence of bond cleavage and crosslinking reactions using a Monte Carlo statistical approach (30-34). A similar statistical approach for coal decomposition using percolation theory has been presented by Grant et al. (35). Such statistical methods have been used for the inverse problem in the polymer literature, i.e., the formation of a macromolecular network by polymerization (36-40).

EXPERIMENTAL

SAMPLES - Samples of bituminous and subbituminous coal were provided by the Penn State Coal Sample Bank and the Argonne Premium Sample Bank. The Penn State coals were obtained undried and in lump form about 12 mm diameter and were crushed in a glove box under oxygen-free nitrogen to 0.8 mm top size. The crushed coals were subdivided by riffing into a number of 10 g representative samples and sealed in vials under nitrogen. The Argonne coals were provided in sealed vials under argon. Properties of the coals are shown in Table 1.

Preliquefaction and Liquefaction Experiments - Preliquefaction and liquefaction experiments were carried out at Penn State University and at Advanced Fuel Research, Inc. The procedure was that described by Derbyshire et al. (6). The preliquefaction was carried out in a tubing bomb at temperatures between 275 and 350°C. Coal was impregnated with MoS₂ catalyst and mixed in a

ratio of 1:2 with liquefaction solvent. In most of the experiments, naphthalene was selected as the solvent. Reactions were carried out in tubing bomb reactors of about 20 cm³ capacity which were heated by immersion in a fluidized sandbath.

Following preliquefaction, the bomb was cooled and vented to determine the gases evolved by volumetric measurement and gas chromatographic analysis. The solid and liquid products were worked-up to obtain the yields of insoluble residue (either chloroform or tetrahydrofuran (THF) insoluble), asphaltenes (hexane insoluble, THF-soluble) and oils (hexane-soluble). In these calculations, it was assumed that the naphthalene was part of the hexane solubles.

ANALYSES - Quantitative FT-IR Analysis - Selected samples of the liquefaction products, total product, the chloroform extracts, the asphaltenes, and the solid residues were analyzed as KBr pellets by FT-IR. The methods employed for quantitative analysis have been described previously (13-16).

TG-FT-IR - Pyrolysis analyses were performed on the preliquefaction solids using thermogravimetric (TG) analysis with on-line analysis of the evolved products (including an infrared spectrum of the condensables) by FT-IR. The TG-FTIR method has been described previously (22,23).

Solvent Swelling and Extraction - The residue samples were extracted with pyridine at the boiling point to obtain the amount and composition of the extract. A portion of the dried, extracted solids was swelled in pyridine in order to estimate the density of crosslinks introduced by the liquefaction process. The solvent swelling measurements were carried out according to the method of Green, Kovac, and Larsen (28,29).

FIMS Analysis - Selected extracts were sent for analysis in the Field Ionization Mass Spectrometry (FIMS) apparatus at SRI International. This technique was described by St. John, et al. (24) and has been used extensively in our development of the network model for coal decomposition (30-34,41,42). The Field Ionization induces little fragmentation and so provides a determination of the sample's molecular weight.

NMR - NMR analyses were performed on selected samples using dipolar dephasing and off magic angle spinning methods developed at the University of Utah (17-21). This work was performed at the University of Utah under the direction of Professor Ronald Pugmire.

Model Compounds - Model compounds were employed to provide well known materials to study specific chemical reactions or to provide standards to calibrate the analytical techniques. These included 1-naphthoic acid and 2-naphthoic acid to study the reaction of aryl carboxyl groups under preliquefaction conditions.

RESULTS

PRODUCTS DISTRIBUTION - Both the products of the preliquefaction and liquefaction stages were analyzed. Variations were made in coal type, (lignite, subbituminous, and bituminous), preliquefaction temperature (275-350°C), gases present (hydrogen, nitrogen, helium), catalyst (Mo or none), solvent (naphthalene, tetralin or dry) preliquefaction time (30 min - 60 min), and liquefaction time at 425°C (10 min - 30 min). Results for PSOC 1401 (a Wyodak subbituminous, which was the most frequently studied coal) are presented in Fig. 1. The figure compares liquefaction data (10 min at 425°C) for no preliquefaction, preliquefaction at 275°C (with H₂ and catalyst) and preliquefaction at 350°C (with H₂ and catalyst). The results show that preliquefaction at 350°C does have a positive effect on the total yield and product quality in liquefaction (much lower residue) while preliquefaction at 275°C causes a negative effect (higher residue). The results for other coals and conditions are summarized as follows:

- 1) Preliquefaction at 275°C appears to have a negative effect on subsequent liquefaction when compared to results without a preliquefaction step. Preliquefaction results in up to 10% of the coal converted to gases and chloroform solubles. Most coals behaved the same and there was little effect due to the presence of either the catalyst or hydrogen.

The solvent was, however, necessary to produce the chloroform extracts as none were produced by a thermal treatment in the absence of a solvent.

- 2) Preliquefaction at 350°C in the presence of a catalyst appears to have a strong positive effect on liquefaction for low rank coals. The largest change due to preliquefaction (high chloroform extract yield, high CO₂ yield) is produced by both hydrogen and catalyst. Nitrogen and catalyst produce smaller but similar changes, while no catalyst produces much less change and as shown by Derbyshire et al. (6) produces little change in liquefaction. Preliquefaction with no solvent or catalyst produces the least change in the product. Preliquefaction in tetralin produces no improvement over preliquefaction in naphthalene.

FT-IR FUNCTIONAL GROUP ANALYSIS - Quantitative FT-IR functional group analysis was performed on the starting coals, preliquefaction residua, chloroform extracts, oils, and asphaltenes.

Residua - Results for PSOC 1401, preliquefaction with H₂ and Mo at 350°C, are presented in Fig. 2. The preliquefaction step produces the following changes: 1) decreases the carbonyl (1700 cm⁻¹) and hydroxyl regions (3400 cm⁻¹) (presumably carboxyl loss); 2) decreases the aliphatic hydrogen (2900 cm⁻¹); and 3) substantially increases the aromatic hydrogen (750-850 cm⁻¹).

The quantitative functional group analysis for PSOC 1401 from these and other spectra are summarized in Fig. 3 and Table 2. The aliphatic hydrogen (Fig. 3a) is found to decrease for solvent treated residues compared to residues formed in the absence of the solvent. The most drastic changes are in the aromatic hydrogen (Fig. 3b), the carbonyl (Fig. 3e), and the one adjacent aromatic hydrogen (Fig. 3g). As can be seen, the major changes are brought about with the catalyst and solvent. These are changes which presumably lead to the improved liquefaction yields.

There are three other cases of interest. The first is HCD 1401-350* which is identical to HC 1401-350* in using hydrogen and a catalyst but no solvent was present. The quantitative functional group analysis is presented in Table 2. It shows the loss in aliphatics and carboxyl, but not the same dramatic increase in the aromatic hydrogen. The second case is NCT 1401-350 which was preliquefied in tetralin with a catalyst under a nitrogen atmosphere. The results in Table 2 are very similar to HCD 1401-350 (low aliphatics and low carboxyl). The third case is for the HC 1401-350 residue after it was subsequently heated to 400°C. This was done to see whether the high aromatic peaks are due to adsorbed naphthalene. The data in Table 2 show that the functional group composition is almost identical to that in the starting residue. So heating to 400°C does not change the chemistry and adsorbed naphthalene is not likely.

Our initial conclusion from the FT-IR data on the residua is that it is the reduction in the carboxyl concentration which is most important to the improvements brought about by preliquefaction, and this reduction requires the catalyst but not the solvent and probably not the hydrogen. The major reasons for these conclusions are: 1) pretreatments dry, with naphthalene (with hydrogen and nitrogen) and with tetralin, all reduced the carboxyl concentration, and the dry and naphthalene cases both produced improved liquefaction yields; 2) the presence of hydrogen does not appear to make much difference between HC 1401-350 and NC 1401-350; and 3) the increased aromatics were not present in the dry preliquefaction residue (HCD 1401-350) and so, do not appear necessary for the improvement in liquefaction.

The increase in the aromatic hydrogen appears to result from adducted naphthalene for the following reasons: 1) the peak positions are consistent with adducted naphthalene; 2) the increase is too large to have come from conversion of aliphatic hydrogen to aromatic hydrogen, no increase was seen for NT 1401-350 which had a similar decrease in aliphatic hydrogen; 3) increased aromatic hydrogen due to removal of the carboxyls would not be likely to increase the one adjacent hydrogen peak; and 4) the peak must be due to a tightly bound chemical because it is not removed at 400°C.

Extracts - Quantitative spectra were obtained for the soluble products of the preliquefaction process. Results for the THF extracts of the residue (asphaltene 1) for HC 1401-350 is presented in Fig. 4 and Table 2. The asphaltenes are very high in carboxyl groups, methyl groups, and aliphatic or

hydroaromatic hydrogen. The spectrum does not show very large aromatic peaks; the material appears to contain less than 50% aromatic carbon based on the amount of aliphatic carbon and oxygen present. The THF solubles appear to have carboxyl concentration comparable to the original coal but much larger than the residue. They contain significantly less ether oxygen.

TG-FTIR ANALYSIS - The analysis of the volatile products are related to the functional group composition of the sample, so the TG-FTIR analysis provides a good complement to the FT-IR functional group analysis. Since the FT-IR analysis showed the carbonyl region to change drastically in preliquefaction, we consider the CO_2 evolution which results from the thermal decomposition of the carboxyl groups. Figure 5 compares the CO_2 evolution from a number of residua. The major change occurs for the catalytic preliquefaction at 350°C (HC 1401-350 and NC 1401-350). Here a drastic reduction is observed in the CO_2 evolution at all temperatures. **This suggests a major chemical change in the carboxyl groups.** The nitrogen thermal case shows less of a change.

SOLVENT SWELLING - The results showed that there was less or comparable loss in solvent swelling for a catalytic preliquefaction compared to thermal treatment without a catalyst. But since the catalytically treated samples show much greater removal of the carboxyl groups, these samples will undergo much less crosslinking upon further thermal treatment.

FIMS ANALYSES - FIMS analyses were performed on the extracts from HC 1401-350 which were separated into hexane solubles (oils plus naphthalenes) and hexane insoluble, THF soluble (asphaltene 2). The oil fraction is very volatile with an average molecular weight of 303 AMU on a number average basis. **The results show that there is significant chemistry going on involving naphthalene dimerization and probably addition.**

NMR ANALYSIS - NMR analysis was performed on the residue from HC 1401-350. The results are presented in Table 3. The data confirm the lower aliphatic content and higher aromatic content in the preliquefaction samples determined in FT-IR. The increase in the aromatic content is in protonated carbon (0.28 for the residue compared to 0.17 for the coal). The major decrease in the aliphatics is in the CH_2 groups (0.27 in the coal vs. 0.16 in the residue). The cluster size in the preliquefaction coal (12.3 carbons) appears to be higher than for the raw coal (9.7). The carboxyl carbon (F_a) in the preliquefaction product (0.05) is also lower than in the raw coal (0.08) consistent with the FT-IR and TG-FTIR results.

STUDIES WITH MODEL COMPOUND - Since the results of the preliquefaction experiments with a subbituminous coal at 350°C in the presence of a catalyst showed a significant role of carboxyl groups in preliquefaction chemistry, model compounds with aryl carboxyl groups (1-naphthoic acid and 2-naphthoic acid) were studied. The preliquefaction was carried out at 350°C for 1 hour in nitrogen with ammonium tetrathiomolybdate (1% Mo on dmmf basis) as the catalyst. The starting reaction mixture used was 50% naphthalene, 25% of 1-naphthoic acid and 25% of 2-naphthoic acid (weight basis). The FT-IR spectra (dry, uncorrected) of the starting reaction mixture and the residue after preliquefaction were compared. There is a strong loss in the carbonyl and hydroxyl bands due to the loss of carboxyl groups during the preliquefaction in the presence of the catalyst. A blank run was done without the catalyst which indicates that the catalyst is necessary to cause excessive decarboxylation. The CO_2 formation was more than a factor of three higher, due to the presence of the catalyst. The CO_2 evolution in absence of the catalyst is due to the higher decarboxylation.

MODELING

The liquefaction model is based on AFR's FG-DVC model of coal devolatilization (30-32). The model describes the decomposition or condensation of the macromolecular network under the influence of bond breaking and crosslinking reactions. Our model employs a sample macromolecular network in the computer consisting of aromatic ring clusters (monomers) linked by bridges. The bridges are either broken by bond scission reactions or are formed by crosslinking. In the model, the break-up or solidification of the molecule occurs near a "gel point" where the number of unbroken bonds per ring cluster (monomer), α , reaches a critical value $\alpha_c \approx 0.95$. For bituminous coals, this critical value can be achieved in pyrolysis and the coal melts and becomes fluid. The effects of low temperature crosslinking which occurs for low rank coals is to increase α so that in some cases the network

cannot come apart by normal pyrolytic reactions.

For liquefaction, the hydrogen consumption in the pyrolysis process (which required hydrogen donation from the aliphatic and hydroaromatic hydrogen in the coal) was modified to allow donation from the solvent. In addition, the external and internal transport steps in devolatilization (which describe vaporization of small molecules and gas phase transport) are modified to describe small molecules becoming liquid and mixing with the solvent. The details of AFR's FG-DVC model can be found in Ref. 32.

From the analysis of the results on the preliquefaction chemistry, it was found that the preliquefaction process results in reduction of carboxyl groups, partial crosslinking of the structure and some bond breaking resulting in higher chloroform extractables. The effect of this preliquefaction process on subsequent liquefaction is high yields of liquids.

The preliquefaction chemistry and its effect on subsequent pyrolysis were simulated by the FG-DVC model. The starting polymer structure of Wyodak coal was modified by putting additional crosslinks (0.13/monomer) to account for partial crosslinking of the structure. The original coal had pyridine solubles of 7.4% but the residue after preliquefaction has THF solubles of 21.5%. To account for this change in the molecular weight distribution of the starting polymer, the oligomer length was decreased from 10 to 4. The donatable hydrogen was kept constant in both cases. The carboxy content (responsible for early crosslinking) was reduced from 6.9% to 2.9%. The results of the simulation are shown in Fig. 8.

Comparing Figs. 8a and 8c for the original and modified coals respectively, we find that while the number of bonds/bead α for the unmodified coal do not go below the critical value of 0.95, the value of α for the modified coal does. This results in the opening of the macromolecular structure and better penetration of the liquefaction solvent in subsequent liquefaction resulting in high liquid yields. Figures 8b and 8d compare the fluid fraction of the mixture on pyrolysis at 440°C for original and modified coals respectively. The modified coal shows a much higher fluid fraction which results in greater fluidity during subsequent liquefaction.

DISCUSSION

There are three suggested modifications which could lead to improved liquefaction. They are: 1) reduced crosslinking; 2) hydrogenation; and 3) increased bond breaking. The experimental results suggest that modification 1 is the most likely, 2 does not occur and 3 appears to happen to some extent.

Having identified the probable chemical changes responsible for improvements in yield and quality in liquefaction, attention was focused on the reactions which produce the chemical changes. The results raise the following questions and possible answers.

Question 1. What is the chemistry of carboxyl removal? Partial answer. **There are carboxyls removed from the residue by conversion to CO₂ and with the extract.** This occurs only in the presence of the catalyst but with or without the solvent or hydrogen. Fewer crosslinks are formed than would otherwise have been formed with the amount of carboxyl removed. This is confirmed by FT-IR, TG-FTIR, NMR, the model simulation, and experiments with model compounds. Naphthalene adduction could have occurred in the HC 1401-350 case to produce the high aromatic, but carboxyl removed occurred in other cases without this effect. Most of the carboxyl removed is by the formation of CO₂. Decarboxylation is seen for the model compounds in the presence of the catalyst.

Question 2. What happens to aliphatics? The most probable answer. **There is a reduction in the aliphatics, most likely produced by removal (with the chloroform solubles) of long chain polymethylene and small fragments high in methyl.** This is confirmed by FT-IR, TG-FTIR, and NMR.

Question 3. Where do the increased aromatics come from? The most probable answer. **Large increases in aromatics were observed in some cases, which are probably due to naphthalene**

adduction. Conversion from aliphatics is unlikely. The evidence comes from FT-IR, NMR, FIMS and the model compound studies which show that naphthalene adduction occurs.

Question 4. What kind of bonds hold the preliquefaction insoluble products together? The most probable answer. **The bonds remaining in the residue appear similar to those in the parent coal based on the liquefaction and TG-FTIR data.** But there is no really good experiment which determines the kinds of bonds. Based on the FT-IR spectra of the residue there is enough aliphatic hydrogen for $-\text{CH}_2\text{CH}_2-$ bonds.

Question 5. Why is the preliquefied insoluble product so easily liquefied? The most probable answer. **The preliquefaction product with the reduced carboxyl groups content is more easily liquefied than the parent coal.** Based on the product distribution and solvent swelling data and the model simulation, this improvement results from a reduction in the CO_2 associated crosslinks and from the bond breaking which produces the chloroform solubles. Both effects reduce the total number of bonds linking the network so that the coal can become fluid. If the chloroform soluble fraction is removed after preliquefaction and the residue liquefied, the drastic improvement in the liquefaction is not observed. The model simulation confirms that the residue alone will liquefy slightly better than the parent coal, but not as good as the mixture.

CONCLUSIONS

- 1) Preliquefaction of a Wyodak subbituminous coal at 350°C with solvent, catalyst and hydrogen produced the best results, (highest yields and best quality) in subsequent liquefaction for 10 minutes. The preliquefaction step produced substantial changes in the functional group composition of the residue, (low aliphatic, low carboxyl, and high aromatic), a large chloroform extract yield and a high CO_2 yield.
- 2) Other preliquefaction treatments at 350°C produced results which were not as good as the best case.
- 3) The preliquefaction step did not appear to induce appreciable hydrogenation of the residue even with tetralin as a solvent or a hydrogen gas atmosphere.
- 4) The improvement in liquefaction behavior appears to be due to loss of the functional groups usually responsible for crosslinking without the associated crosslink formation; probably carboxyl.
- 5) Experiments were carried out to test whether carboxyl groups on a model compound were removed under preliquefaction conditions (350°C , Mo, naphthalene solvent and nitrogen or hydrogen gas). Results showed that almost all of the carboxyl groups were converted to CO_2 . Almost no decarboxylation occurred in the absence of the catalyst.
- 6) Simulations show that the reduction in the carboxyl group concentration in the preliquefaction step for the Wyodak coal is capable of significantly enhancing the subsequent decomposition of the macromolecular network in the liquefaction step, thus improving the liquefaction yields.

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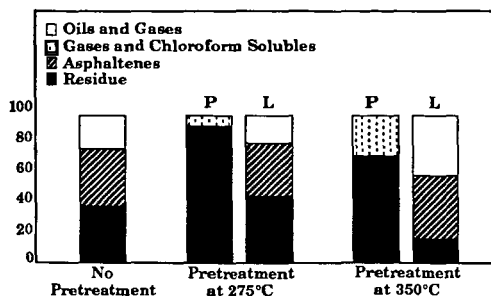


Figure 1. Product Distributions for Preliquefaction and Liquefaction Comparing Results for No Preliquefaction, Preliquefaction at 275°C and Preliquefaction at 350°C. P = Pretreatment and L = Liquefaction. Liquefaction Conditions - 425°C, Mo, Catalyst, Naphthalene Solvent, Hydrogen, Atmosphere (10 min.). Preliquefaction Conditions - Mo, Catalyst, Naphthalene Solvent, Hydrogen, Atmosphere (275°C - 30 min., 350°C - 60 min.).

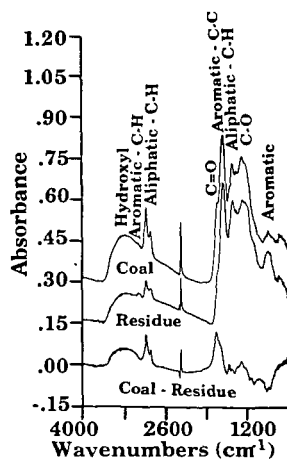


Figure 2. Comparison of FT-IR Spectra for Residue and Parent Coal for PSOC-1401 Wyodak Subbituminous Coal.

Table 1 - Coal Properties.

Coal	PSOC-1504	PSOC-1401	PSOC-1482	Beulah Zap	Wyodak
Seam	Upper Sunnyside	Lower Wyodak	Hagel	Beulah Zap	Wyodak-Anderson
State	Utah	Wyoming	North Dakota	North Dakota	Wyoming
ASTM Rank Class (apparent)	HVA	Subbituminous	Lignite	Lignite	Subbituminous
Moisture Content (wt. % (a.r.))	3.4	16.3	34.5	32.2	28.1
Mineral Matter	8.6	6.5	9.7	11.1	10.0
Elemental Composition Wt.% dmmf					
C	82.9	72.7	72.2	74.1	76.0
H	5.8	4.5	4.4	4.9	5.4
O ^a	8.7	21.4	21.6	19.1	17.0
N	1.8	1.1	1.1	1.2	1.1
S	0.8	0.3	0.7	0.7	0.5
Sulphur Forms (% dry coal)					
Organic	0.71	0.26	0.61	0.63	0.43
Pyritic	0.04	0.01	0.09	0.14	0.17
Sulphate	0.02	0.00	0.02	0.03	0.03
Total	0.77	0.27	0.72	0.80	0.63

^a by Difference

Table 2. Quantitative FT-IR Analysis of PSOC-1401 Residues at 350°C. (wt. % dimmf)

Sample	Hydrogen				Aromatic Hydrogen			Carbon	Carbonyl	Oxygen				
	H _{al}	H _h	H _{ar}	H _{total}	H _{ar} /H _{total}	1Adj	2Adj	3 +	C _{al}	Units (Abs. x cm ⁻¹)	O _h	O _{ether}	O _{total}	
PSOC-1401	DP1401.000	2.57	.37	1.44	4.38	.33	.40	.74	.30	17.13	31.33	5.96	4.88	10.84
PSOC-1401	DP1401.001	2.85	.36	1.49	4.70	.32	.47	.65	.37	19.00	33.32	5.74	5.40	11.14
HC1401-350	H1401D.000	1.54	.25	2.27	4.06	.56	1.07	.82	.38	10.27	13.03	4.00	5.25	9.25
HC1401-350	H11401D.001	1.50	.26	2.39	4.15	.58	.93	.99	.47	10.00	13.73	4.10	6.25	10.35
HC1401-350	AF374D.000	1.25	.23	2.64	4.12	.64	.99	1.19	.46	8.33	12.89	3.75	6.00	9.75
HC1401-350	AF374D.001	1.37	.23	2.27	3.87	.59	.80	1.04	.43	9.13	12.83	3.75	6.40	10.15
NC1401-350	N1401D.000	1.29	.28	2.14	3.71	.58	.79	.92	.43	8.60	16.15	4.50	4.75	9.25
NC1401-350	N1401D.001	1.22	.30	2.29	3.81	.60	.88	1.01	.40	8.13	18.50	4.75	5.25	10.00
NT1401-350	ALRCD2.000	1.42	.41	1.57	3.40	.46	.46	.65	.46		24.81	6.50	9.00	15.50
NT1401-350	ALRCD2.001	1.10	.42	1.26	2.79	.45	.34	.59	.33	7.33	20.91	6.75	6.50	13.25
NC1401-350Tet	ALRCD0.005	1.82	.18	1.70	3.70	.46	.57	.78	.35	12.13	12.94	2.90	5.50	8.40
NC1401-350Tet	ALRCD1.005	2.04	.22	1.63	3.89	.42	.48	.68	.47	13.60	13.60	3.60	5.60	9.20
HeD1401-350	T1401D.000	2.03	.25	1.37	3.65	.38	.38	.69	.30	13.53	31.82	4.00	6.00	10.00
HeD1401-350	T1401D.001	2.07	.25	1.27	3.59	.35	.36	.64	.27	13.80	31.09	4.00	6.00	10.00
HCD1401-350	HCNSID.000	2.09	.14	1.30	3.53	.37	.38	.61	.31	13.93	12.73	2.20	6.40	8.60
HCD1401-350	HCNSID.001	2.38	.16	1.59	4.13	.38	.53	.68	.38	15.87	12.49	2.60	6.90	9.50
HC1401-350		7.01	.51	1.18	8.70	.14	.35	.35	.48	46.73	25.30	8.20	2.50	10.70
HC1401-350		6.60	.51	1.27	8.38	.15	.40	.36	.51	44.00	22.21	8.20	2.10	10.30

Nomenclature

HC - Hydrogen Catalytic
 NC - Nitrogen Catalytic
 HT - Hydrogen Thermal
 NT - Nitrogen Thermal
 HCD - Hydrogen Catalytic Dry
 HeD - Helium Dry
 Tet - Tetralin

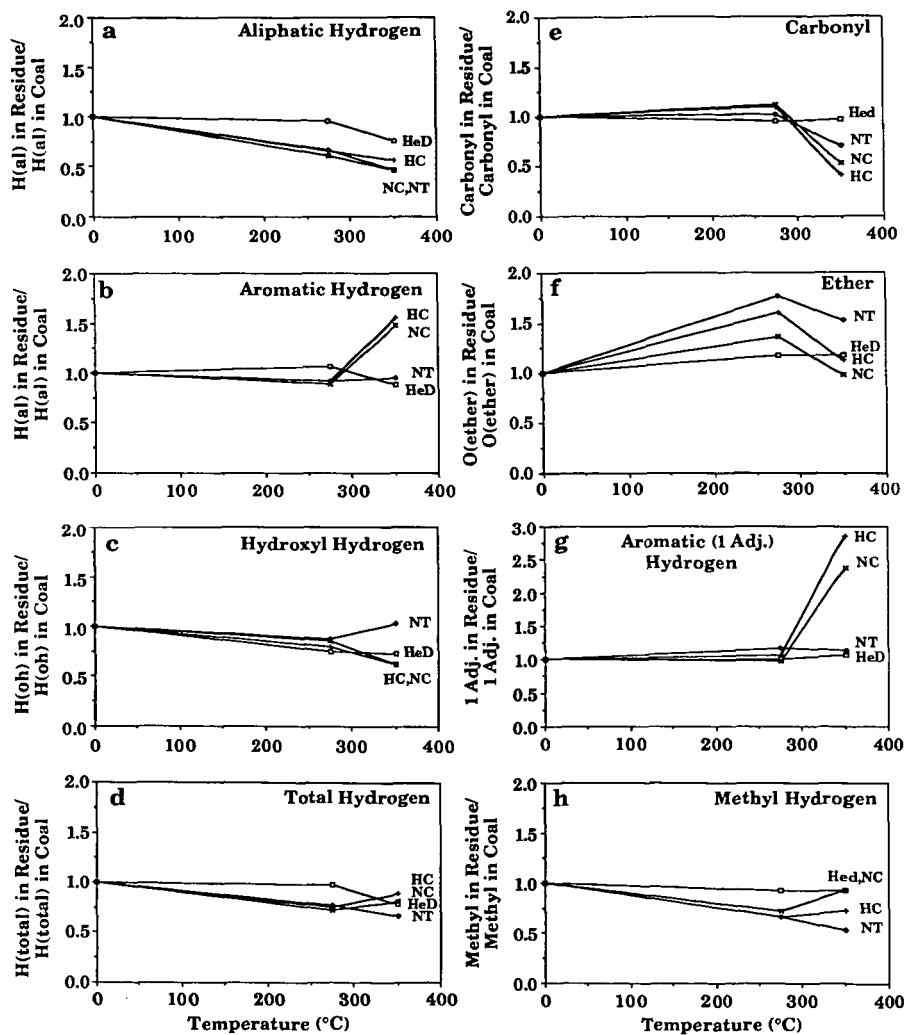


Figure 3. Variations in Functional Group Compositions with Preliquefactions.

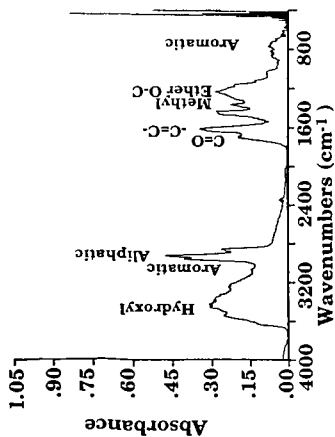


Figure 4. Comparison of FT-IR Spectra of THF Extracts of the Residue (Asphaltene) Formed at 350°C in the Presence of Catalyst and the Presence of Hydrogen.

Table 3 - Carbon Structural Distribution of the Wyodak Subbituminous Coal and the Preliquefaction Residue Formed at 350°C in the Presence of Catalyst and Hydrogen

Sample	f_a	f_a^C	f_a^H	f_{al}	f_{al}^H	f_{al}^*	Carbons/Clusters
Coal	.63	.08	.17	.37	.27	.10	9.7
Char	.75	.05	.28	.25	.16	.09	12.3

Fractions of sp^2 hybridized carbon and (error estimate).

- f_a = total carbon. (± 0.03).
- f_a^C = carbonyl - $\delta > 165$ ppm. (± 0.02).
- f_a^H = protonated and aromatic. (± 0.03).
- Fraction of sp^3 hybridized carbon and (error estimate).
- f_{al} = total carbon (± 0.02).
- f_{al}^H = CH or CH₂. (± 0.02).
- f_{al}^* = CH₃ or nonprotonated. (± 0.03).

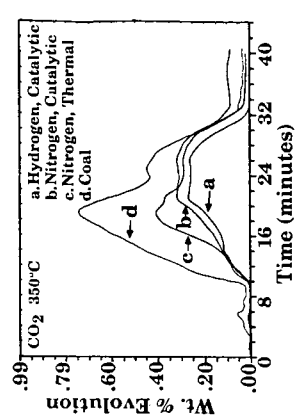


Figure 5. Comparison of CO₂ Evolution Profiles for PSOC-1401 Samples of Coal and Preliquefaction Residue at 350°C from the TG-Plus.

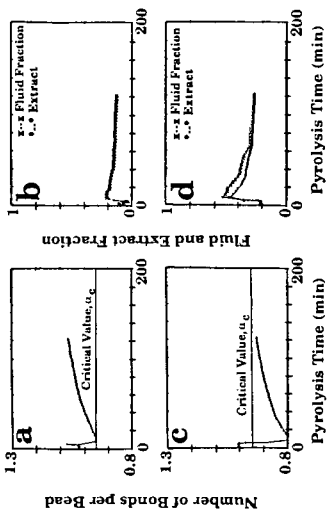


Figure 6. Comparison of Number of Bonds per Bead for a) Original Wyodak Coal (initial crosslinks = 290, initial extract yield = 7.4%, oligomer length = 10 and hard bonds = 200) and c) Modified Wyodak Coal (initial crosslinks = 600, initial extract yield = 21.5%, oligomer length = 4 and hard bonds = 0). b and d Compare the Fluid Fraction and Extract Yield for Original Wyodak Coal and Modified Wyodak Coal, Respectively.